

## PCT

### NOTIFICATION OF ELECTION

(PCT Rule 61.2)

From the INTERNATIONAL BUREAU

To:

Assistant Commissioner for Patents  
United States Patent and Trademark  
Office  
Box PCT  
Washington, D.C. 20231  
ETATS-UNIS D'AMERIQUE

in its capacity as elected Office

Date of mailing: <div style="text-align: center;">11 May 2000 (11.05.00)</div>	
International application No.: <div style="text-align: center;">PCT/EP99/07941</div>	Applicant's or agent's file reference: <div style="text-align: center;">D-42992-01</div>
International filing date: <div style="text-align: center;">19 October 1999 (19.10.99)</div>	Priority date: <div style="text-align: center;">29 October 1998 (29.10.98)</div>
Applicant: <div style="text-align: center;">PALEARI, Mario et al</div>	

1. The designated Office is hereby notified of its election made:

☒ in the demand filed with the International preliminary Examining Authority on:  

09 February 2000 (09.02.00)

☐ in a notice effecting later election filed with the International Bureau on:  

\_\_\_\_\_

2. The election ☒ was

☐ was not

made before the expiration of 19 months from the priority date or, where Rule 32 applies, within the time limit under Rule 32.2(b).

<p style="text-align: center;">The International Bureau of WIPO 34, chemin des Colombettes 1211 Geneva 20, Switzerland</p> <p>Facsimile No.: (41-22) 740.14.35</p>	<p>Authorized officer:</p> <p style="text-align: center;">J. Zahra</p> <p>Telephone No.: (41-22) 338.83.38</p>
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## PATENT COOPERATION TREATY

From the  
INTERNATIONAL PRELIMINARY EXAMINING AUTHORITY

To:

DE CARLI, Elda  
CRYOVAC S.P.A.  
Via Trento 7  
I-20017 Passirana di Rho (Milan)  
ITALIE

PCT

NOTIFICATION OF TRANSMITTAL OF  
THE INTERNATIONAL PRELIMINARY  
EXAMINATION REPORT  
(PCT Rule 71.1)

Date of mailing  
(day/month/year) 15.06.2000

Applicant's or agent's file reference  
D-42992-01

IMPORTANT NOTIFICATION

International application No.  
PCT/EP99/07941

International filing date (day/month/year)  
19/10/1999

Priority date (day/month/year)  
29/10/1998

Applicant  
CRYOVAC, INC. et al.


1. The applicant is hereby notified that this International Preliminary Examining Authority transmits herewith the international preliminary examination report and its annexes, if any, established on the international application.
2. A copy of the report and its annexes, if any, is being transmitted to the International Bureau for communication to all the elected Offices.
3. Where required by any of the elected Offices, the International Bureau will prepare an English translation of the report (but not of any annexes) and will transmit such translation to those Offices.
4. REMINDER

The applicant must enter the national phase before each elected Office by performing certain acts (filing translations and paying national fees) within 30 months from the priority date (or later in some Offices) (Article 39(1)) (see also the reminder sent by the International Bureau with Form PCT/IB/301).

Where a translation of the international application must be furnished to an elected Office, that translation must contain a translation of any annexes to the international preliminary examination report. It is the applicant's responsibility to prepare and furnish such translation directly to each elected Office concerned.

For further details on the applicable time limits and requirements of the elected Offices, see Volume II of the PCT Applicant's Guide.

Name and mailing address of the IPEA/

 European Patent Office  
D-80298 Munich  
Tel. +49 89 2399 - 0 Tx: 523656 epmu d  
Fax: +49 89 2399 - 4465

Authorized officer

Ridé, M-C

Tel. +49 89 2399-8082



## PATENT COOPERATION TREATY

## PCT

## INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)

Applicant's or agent's file reference D-42992-01	FOR FURTHER ACTION See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416)	
International application No. PCT/EP99/07941	International filing date (day/month/year) 19/10/1999	Priority date (day/month/year) 29/10/1998
International Patent Classification (IPC) or national classification and IPC B32B27/08		
Applicant CRYOVAC, INC. et al.		

1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.



2. This REPORT consists of a total of 4 sheets, including this cover sheet.

- ☐ This report is also accompanied by ANNEXES, i.e. sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).

These annexes consist of a total of sheets.

3. This report contains indications relating to the following items:

- I ☒ Basis of the report
- II ☐ Priority
- III ☐ Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
- IV ☐ Lack of unity of invention
- V ☒ Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability: citations and explanations supporting such statement
- VI ☐ Certain documents cited
- VII ☐ Certain defects in the international application
- VIII ☐ Certain observations on the international application

Date of submission of the demand  09/02/2000	Date of completion of this report  15.06.2000
Name and mailing address of the international preliminary examining authority:   European Patent Office D-80298 Munich Tel. +49 89 2399 - 0 Tx: 523658 epmu d Fax: +49 89 2399 - 4465	Authorized officer  Schambeck, W  Telephone No. +49 89 2399 2135 

**INTERNATIONAL PRELIMINARY  
EXAMINATION REPORT**

International application No. PCT/EP99/07941

**I. Basis of the report**

1. This report has been drawn on the basis of *(substitute sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to the report since they do not contain amendments.)*:

**Description, pages:**

1-30 as originally filed

**Claims, No.:**

1-10 as originally filed

2. The amendments have resulted in the cancellation of:

- ☐ the description, pages:  
☐ the claims, Nos.:  
☐ the drawings, sheets:

3. ☐ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)):

4. Additional observations, if necessary:

**V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement****1. Statement**

Novelty (N)	Yes: Claims 4-10
	No: Claims 1-3
Inventive step (IS)	Yes: Claims 4-10
	No: Claims 1-3
Industrial applicability (IA)	Yes: Claims 1-10
	No: Claims

**INTERNATIONAL PRELIMINARY  
EXAMINATION REPORT**International application No. PCT/EP99/07941

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**2. Citations and explanations**

see separate sheet

**INTERNATIONAL PRELIMINARY**

International application No. PCT/EP99/07941

**EXAMINATION REPORT - SEPARATE SHEET**

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1. The inventions defined by claims 1 to 3 are to be regarded as lacking novelty and an inventive step because EP-A-0 107 854 discloses multi-layer heat-shrinkable films falling within the scope of protection conferred by those claims.

Attention is drawn, by way of explanation of this statement, to examples 1 to 4 and 7 of the prior art document and to the fact that the polyolefin and the polyamide layers of the multi-layer films described in those examples are considered to inevitably provide, at least to a certain extent, heat-sealability and abuse resistance, respectively (although those properties may not have been aimed at by the authors of the prior art document).

2. The inventions defined by claims 4 to 10 are to be regarded as novel and involving an inventive step because no disclosure can be found in the documents cited in the search report of subject-matter covered by the wording of those claims, let alone a suggestion that the problem identified in the description of the application under examination, page 1, line 24 to page 2, line 12 could be solved by the claimed teaching.

## ATENT COOPERATION TREATY

From the INTERNATIONAL SEARCHING AUTHORITY

**PCT**NOTIFICATION OF TRANSMITTAL OF  
THE INTERNATIONAL SEARCH REPORT  
OR THE DECLARATION

(PCT Rule 44.1)

To:

CRYOVAC S.P.A.  
Attn. De Carli, Elda  
Via Trento 7  
I-20017 Passirana di Rho (Milan)  
ITALYDate of mailing  
(day/month/year)

21/01/2000

Applicant's or agent's file reference

D-42992-01

FOR FURTHER ACTION

See paragraphs 1 and 4 below

International application No.

PCT/EP 99/07941

International filing date  
(day/month/year)

19/10/1999

Applicant

CRYOVAC, INC. et al.

- 1.
- ☒
- The applicant is hereby notified that the International Search Report has been established and is transmitted herewith.

Filing of amendments and statement under Article 19:

The applicant is entitled, if he so wishes, to amend the claims of the International Application (see Rule 48):

When? The time limit for filing such amendments is normally 2 months from the date of transmittal of the International Search Report; however, for more details, see the notes on the accompanying sheet.

Where? Directly to the International Bureau of WIPO  
34, chemin des Colombettes  
1211 Geneva 20, Switzerland  
Facsimile No.: (41-22) 740.14.35

For more detailed instructions, see the notes on the accompanying sheet.

- 2.
- ☐
- The applicant is hereby notified that no International Search Report will be established and that the declaration under Article 17(2)(a) to that effect is transmitted herewith.

- 3.
- ☐
- With regard to the protest against payment of (an) additional fee(s) under Rule 40.2, the applicant is notified that:

☐ the protest together with the decision thereon has been transmitted to the International Bureau together with the applicant's request to forward the texts of both the protest and the decision thereon to the designated Offices.☐ no decision has been made yet on the protest; the applicant will be notified as soon as a decision is made.

4. Further action(s): The applicant is reminded of the following:

Shortly after 18 months from the priority date, the International application will be published by the International Bureau. If the applicant wishes to avoid or postpone publication, a notice of withdrawal of the International application, or of the priority claim, must reach the International Bureau as provided in Rules 90bis.1 and 90bis.3, respectively, before the completion of the technical preparations for international publication.

Within 19 months from the priority date, a demand for international preliminary examination must be filed if the applicant wishes to postpone the entry into the national phase until 30 months from the priority date (in some Offices even later).

Within 20 months from the priority date, the applicant must perform the prescribed acts for entry into the national phase before all designated Offices which have not been elected in the demand or in a later election within 19 months from the priority date or could not be elected because they are not bound by Chapter II.

Name and mailing address of the International Searching Authority

European Patent Office, P.B. 5818 Patentlaan 2  
NL-2280 HV Rijswijk  
Tel. (+31-70) 340-2040, Tx. 31 851 epo nl,  
Fax (+31-70) 340-3018

Authorized officer

Alfredo Prein

## NOTES TO FORM PCT/ISA/220

These Notes are intended to give the basic instructions concerning the filing of amendments under article 19. The Notes are based on the requirements of the Patent Cooperation Treaty, the Regulations and the Administrative Instructions under that Treaty. In case of discrepancy between these Notes and those requirements, the latter are applicable. For more detailed information, see also the PCT Applicant's Guide, a publication of WIPO.

In these Notes, "Article", "Rule", and "Section" refer to the provisions of the PCT, the PCT Regulations and the PCT Administrative Instructions respectively.

## INSTRUCTIONS CONCERNING AMENDMENTS UNDER ARTICLE 19

The applicant has, after having received the international search report, one opportunity to amend the claims of the international application. It should however be emphasized that, since all parts of the international application (claims, description and drawings) may be amended during the international preliminary examination procedure, there is usually no need to file amendments of the claims under Article 19 except where, e.g. the applicant wants the latter to be published for the purposes of provisional protection or has another reason for amending the claims before international publication. Furthermore, it should be emphasized that provisional protection is available in some States only.

**What parts of the international application may be amended?**

Under Article 19, only the claims may be amended.

During the international phase, the claims may also be amended (or further amended) under Article 34 before the International Preliminary Examining Authority. The description and drawings may only be amended under Article 34 before the International Examining Authority.

Upon entry into the national phase, all parts of the international application may be amended under Article 28 or, where applicable, Article 41.

**When?**

Within 2 months from the date of transmittal of the international search report or 16 months from the priority date, whichever time limit expires later. It should be noted, however, that the amendments will be considered as having been received on time if they are received by the International Bureau after the expiration of the applicable time limit but before the completion of the technical preparations for international publication (Rule 46.1).

**Where not to file the amendments?**

The amendments may only be filed with the International Bureau and not with the receiving Office or the International Searching Authority (Rule 46.2).

Where a demand for international preliminary examination has been/is filed, see below.

**How?**

Either by cancelling one or more entire claims, by adding one or more new claims or by amending the text of one or more of the claims as filed.

A replacement sheet must be submitted for each sheet of the claims which, on account of an amendment or amendments, differs from the sheet originally filed.

All the claims appearing on a replacement sheet must be numbered in Arabic numerals. Where a claim is cancelled, no renumbering of the other claims is required. In all cases where claims are renumbered, they must be renumbered consecutively (Administrative Instructions, Section 205(b)).

The amendments must be made in the language in which the international application is to be published.

**What documents must/may accompany the amendments?**

**Letter (Section 205(b)):**

The amendments must be submitted with a letter.

The letter will not be published with the international application and the amended claims. It should not be confused with the "Statement under Article 19(1)" (see below, under "Statement under Article 19(1)").

The letter must be in English or French, at the choice of the applicant. However, if the language of the international application is English, the letter must be in English; if the language of the international application is French, the letter must be in French.



## NOTES TO FORM PCT/ISA/220 (continued)

The letter must indicate the differences between the claims as filed and the claims as amended. It must, in particular, indicate, in connection with each claim appearing in the international application (it being understood that identical indications concerning several claims may be grouped), whether

- (i) the claim is unchanged;
- (ii) the claim is cancelled;
- (iii) the claim is new;
- (iv) the claim replaces one or more claims as filed;
- (v) the claim is the result of the division of a claim as filed.

The following examples illustrate the manner in which amendments must be explained in the accompanying letter:

1. [Where originally there were 48 claims and after amendment of some claims there are 51]:  
"Claims 1 to 29, 31, 32, 34, 35, 37 to 48 replaced by amended claims bearing the same numbers; claims 30, 33 and 36 unchanged; new claims 49 to 51 added."
2. [Where originally there were 15 claims and after amendment of all claims there are 11]:  
"Claims 1 to 15 replaced by amended claims 1 to 11."
3. [Where originally there were 14 claims and the amendments consist in cancelling some claims and in adding new claims]:  
"Claims 1 to 6 and 14 unchanged; claims 7 to 13 cancelled; new claims 15, 16 and 17 added."  
"Claims 7 to 13 cancelled; new claims 15, 16 and 17 added; all other claims unchanged."
4. [Where various kinds of amendments are made]:  
"Claims 1-10 unchanged; claims 11 to 13, 18 and 19 cancelled; claims 14, 15 and 16 replaced by amended claim 14; claim 17 subdivided into amended claims 15, 16 and 17; new claims 20 and 21 added."

**"Statement under article 19(1)" (Rule 46.4)**

The amendments may be accompanied by a statement explaining the amendments and indicating any impact that such amendments might have on the description and the drawings (which cannot be amended under Article 19(1)).

The statement will be published with the international application and the amended claims.

It must be in the language in which the international application is to be published.

It must be brief, not exceeding 500 words if in English or if translated into English.

It should not be confused with and does not replace the letter indicating the differences between the claims as filed and as amended. It must be filed on a separate sheet and must be identified as such by a heading, preferably by using the words "Statement under Article 19(1)."

It may not contain any disparaging comments on the international search report or the relevance of citations contained in that report. Reference to citations, relevant to a given claim, contained in the international search report may be made only in connection with an amendment of that claim.

**Consequence if a demand for international preliminary examination has already been filed**

If, at the time of filing any amendments under Article 19, a demand for international preliminary examination has already been submitted, the applicant must preferably, at the same time of filing the amendments with the International Bureau, also file a copy of such amendments with the International Preliminary Examining Authority (see Rule 62.2(a), first sentence).

**Consequence with regard to translation of the international application for entry into the national phase**

The applicant's attention is drawn to the fact that, where upon entry into the national phase, a translation of the claims as amended under Article 19 may have to be furnished to the designated/elected Offices, instead of, or in addition to, the translation of the claims as filed.

For further details on the requirements of each designated/elected Office, see Volume II of the PCT Applicant's Guide.

# PCT

## INTERNATIONAL SEARCH REPORT

(PCT Article 18 and Rules 43 and 44)

Applicant's or agent's file reference <b>D-42992-01</b>	<b>FOR FURTHER ACTION</b> see Notification of Transmittal of International Search Report (Form PCT/ISA/220) as well as, where applicable, item 5 below.	
International application No. <b>PCT/EP 99/ 07941</b>	International filing date (day/month/year) <b>19/10/1999</b>	(Earliest) Priority Date (day/month/year) <b>29/10/1998</b>
Applicant <b>CRYOVAC, INC. et al.</b>		

This International Search Report has been prepared by this International Searching Authority and is transmitted to the applicant according to Article 18. A copy is being transmitted to the International Bureau.

This International Search Report consists of a total of 3 sheets.

☒ It is also accompanied by a copy of each prior art document cited in this report.

### 1. Basis of the report

a. With regard to the **language**, the international search was carried out on the basis of the international application in the language in which it was filed, unless otherwise indicated under this item.

☐ the international search was carried out on the basis of a translation of the international application furnished to this Authority (Rule 23.1(b)).

b. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international search was carried out on the basis of the sequence listing :

☐ contained in the international application in written form.

☐ filed together with the international application in computer readable form.

☐ furnished subsequently to this Authority in written form.

☐ furnished subsequently to this Authority in computer readable form.

☐ the statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.

☐ the statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished

2. ☐ **Certain claims were found unsearchable** (See Box I).

3. ☐ **Unity of invention is lacking** (see Box II).

4. With regard to the **title**,

☒ the text is approved as submitted by the applicant.

☐ the text has been established by this Authority to read as follows:

5. With regard to the **abstract**,

☒ the text is approved as submitted by the applicant.

☐ the text has been established, according to Rule 38.2(b), by this Authority as it appears in Box III. The applicant may, within one month from the date of mailing of this international search report, submit comments to this Authority.

6. The figure of the **drawings** to be published with the abstract is Figure No.

☐ as suggested by the applicant.

☐ because the applicant failed to suggest a figure.

☐ because this figure better characterizes the invention.

☒ None of the figures.

## INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 99/07941

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 B32B27/08 B65D65/40

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 B32B B65D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 447 988 A (GRACE W R & CO) 25 September 1991 (1991-09-25) page 3, line 8 - line 57; claims 1,5-7,17; examples 11,17,19 ---	1,9,10
Y	EP 0 217 252 A (GRACE W R & CO) 8 April 1987 (1987-04-08) *comparative examples 5,6 * page 10; claims; examples 4-10; table III ---	1-3,6-10
Y	EP 0 797 918 A (GUNZE KOBUNSHI CORP) 1 October 1997 (1997-10-01) claims; examples 1,8 ---	1-3,6-10
A	EP 0 277 839 A (KUREHA CHEMICAL IND CO LTD) 10 August 1988 (1988-08-10) * whole, particularly examples 3,4,7 and comparative examples 2,3 * --- -/--	1-9



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

## \* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&amp;" document member of the same patent family

Date of the actual completion of the international search

13 January 2000

Date of mailing of the international search report

21/01/2000

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,  
Fax: (+31-70) 340-3016

Authorized officer

Pamies Olle, S

## INTERNATIONAL SEARCH REPORT

International Application No

PCT/JP 99/07941

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 4 755 402 A (OBERLE TIMOTHY T) 5 July 1988 (1988-07-05) the whole document ---	1,6-10
A	US 4 695 491 A (KONDO KAZUO ET AL) 22 September 1987 (1987-09-22) the whole document ---	1,6-10
A	DATABASE WPI Section Ch, Week 8503 Derwent Publications Ltd., London, GB; Class A18, AN 85-015754 XP002097034 & JP 59 212260 A (SUMITOMO BAKELITE CO), 1 December 1984 (1984-12-01) abstract ---	1-3,7
A	EP 0 107 854 A (KUREHA CHEMICAL IND CO LTD) 9 May 1984 (1984-05-09) examples ---	1-3,6-10
A	WO 98 06574 A (GRACE W R & CO) 19 February 1998 (1998-02-19) claims; examples ---	1-3,6-10
A	GB 2 129 370 A (GRACE W R & CO) 16 May 1984 (1984-05-16) the whole document ---	1-3,10
A	DATABASE WPI Section Ch, Week 9842 Derwent Publications Ltd., London, GB; Class A17, AN 98-481658 XP002099541 & AU 69862 98 A (GRACE & CO-CONN W R), 30 July 1998 (1998-07-30) abstract -----	1-10

# INTERNATIONAL SEARCH REPORT

Info on patent family members

International Application No

PO EP 99/07941

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
EP 0447988	A	25-09-1991	IT 1240341 B	07-12-1993
			IT 1243718 B	21-06-1994
			AT 143855 T	15-10-1996
			AU 638810 B	08-07-1993
			AU 7361591 A	03-10-1991
			CA 2038910 A	24-09-1991
			CS 9100793 A	12-11-1991
			DE 69122535 D	14-11-1996
			DE 69122535 T	13-02-1997
			ES 2092517 T	01-12-1996
			HU 212968 B	30-12-1996
			JP 1931334 C	12-05-1995
			JP 5077861 A	30-03-1993
			JP 6055628 B	27-07-1994
			NZ 237420 A	25-11-1993
			PL 168331 B	29-02-1996
			RU 2085395 C	27-07-1997
EP 0217252	A	08-04-1987	IT 1190394 B	16-02-1988
			IT 1207999 B	01-06-1989
			AT 69427 T	15-11-1991
			AU 582902 B	13-04-1989
			AU 6310286 A	02-04-1987
			BR 8604693 A	23-06-1987
			CA 1303473 A	16-06-1992
			DE 3682473 A	19-12-1991
			DK 170038 B	08-05-1995
			ES 2003111 A	16-10-1988
			FI 863919 A,B,	31-03-1987
			JP 6039978 A	15-02-1994
			JP 7073904 B	09-08-1995
			JP 1944567 C	23-06-1995
			JP 3078065 B	12-12-1991
			JP 62080043 A	13-04-1987
			MX 168438 B	25-05-1993
			NZ 217626 A	28-11-1989
			US RE35285 E	25-06-1996
			US 4801486 A	31-01-1989
EP 0797918	A	01-10-1997	AU 1650397 A	02-10-1997
			CA 2201240 A	29-09-1997
			JP 10004866 A	13-01-1998
			NO 971445 A	30-09-1997
			NZ 314484 A	29-04-1999
EP 0277839	A	10-08-1988	JP 2022052 A	24-01-1990
			AU 585745 B	22-06-1989
			AU 1129988 A	11-08-1988
			DE 3875127 A	12-11-1992
			DE 3875127 T	06-05-1990
			US 4911979 A	27-03-1990
US 4755402	A	05-07-1988	AU 607971 B	21-03-1991
			AU 1265588 A	01-09-1988
			CA 1283268 A	23-04-1991
			JP 2654054 B	17-09-1997
			JP 63224945 A	20-09-1988
			NZ 223339 A	28-05-1990

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/JP 99/07941

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
US 4695491	A	22-09-1987	JP 60259441 A	21-12-1985
JP 59212260	A	01-12-1984	NONE	
EP 0107854	A	09-05-1984	JP 1583122 C	22-10-1990
			JP 2008583 B	26-02-1990
			JP 59079753 A	09-05-1984
			AT 382557 B	10-03-1987
			AT 383883 A	15-08-1986
			AU 2045483 A	03-05-1984
			BE 898125 A	30-04-1984
			CA 1218819 A	10-03-1987
			CH 663576 A	31-12-1987
			DE 3375887 A	14-04-1988
			DK 493283 A,B,	30-04-1984
			ES 526815 A	01-09-1984
			FI 833963 A,B,	30-04-1984
			FR 2535248 A	04-05-1984
			GB 2129737 A,B	23-05-1984
			IT 1169901 B	03-06-1987
			NO 833935 A,B,	30-04-1984
			NZ 206100 A	09-05-1986
			US 4525414 A	25-06-1985
			ZA 8307759 A	29-08-1984
WO 9806574	A	19-02-1998	AU 4061497 A	06-03-1998
			EP 0918635 A	02-06-1999
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<b>(21) International Application Number:</b> PCT/EP99/07941 <b>(22) International Filing Date:</b> 19 October 1999 (19.10.99)  <b>(30) Priority Data:</b> 98120475.3      29 October 1998 (29.10.98)      EP  <b>(71) Applicant (for all designated States except US):</b> CRYOVAC, INC. [US/US]; 100 Rogers Bridge Road, Duncan, SC 29334 (US).  <b>(72) Inventors; and</b> <b>(75) Inventors/Applicants (for US only):</b> PALEARI, Mario [IT/IT]; Via San Francesco, 8, I-20010 Pogliano Milanese (IT). BUZZI, Giampaolo [IT/IT]; Via E. Fermi, 11, I-20017 Rho (IT).  <b>(74) Agent:</b> DE CARLI, Elda; Cryovac S.p.A., Via Trento, 7, I-20017 Passirana Di Rho (IT).		<b>(81) Designated States:</b> AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).  <b>Published</b> <i>With international search report.</i>
<b>(54) Title:</b> NEW HIGH RESISTANCE HEAT-SHRINKABLE THERMOPLASTIC FILM		
<b>(57) Abstract</b> <p>A multi-layer heat-shrinkable film, which is useful in the manufacture of bags with a good balance of mechanical, optical and shrink properties and sealability, comprises an outer heat-sealing layer (a) of a heat-sealable polyolefin, an outer abuse layer (b) comprising a polyamide with a melting temperature <math>\geq 175^{\circ}\text{C}</math>, preferably blended with an ethylene-vinyl alcohol copolymer, and an intermediate gas barrier layer comprising PVDC. The film in the form of a seamless tube wherein the heat-sealing layer (a) is the innermost layer of the tube and the containers, such as bags and pouches, obtained from the film by heat-sealing the heat-sealing layer (a) to itself are also claimed. The bags thus obtained can suitably be heat-sealed also when overlapped.</p>		

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## NEW HIGH RESISTANCE HEAT-SHRINKABLE THERMOPLASTIC FILM

The present invention refers to a multi-layer, heat-shrinkable, thermoplastic film endowed with a desirable balance of properties, including good shrink properties, good optical properties, very good mechanical properties and a peculiar sealability performance.

5 The invention also relates to containers, such as tubing, bags and pouches, made with the film.

In general terms, the packaging of food items by means of a heat-shrinkable, gas- barrier, thermoplastic film comprises configuring the heat-shrinkable packaging material, either partially or completely, around a product (e.g. by placing the food item within a bag or pouch  
10 fabricated from the film), removing excess air from inside the package (e.g. vacuumizing the bag or pouch), sealing it and thereafter exposing the package to a heat source thereby causing the heat-shrinkable film to shrink and conform with the contours of the packaged food.

These films provide to the packaged food an attractive appearance and in the mean time protect the packaged product from the environment and prolong the shelf life of the packaged  
15 product.

These films therefore need to have good gas barrier properties and mainly good sealing properties, in order to guarantee that the atmosphere within the package will not be affected by the atmosphere outside the package; they also need to have high mechanical properties to guarantee that the package will survive the handling involved in the product distribution  
20 chain; finally they also need to have good optical properties and good shrink properties to provide the end package with the attractive appearance.

Packaging films with an adequate balance of the above properties are known in the literature and spread in the market.

A problem that is however often found with the available films is that in the packaging  
25 process it is generally necessary to carefully position the packages to be vacuumized and sealed, one close to the other, in the vacuum chamber, so as to avoid any overlapping of the packages. In fact when overlapped or partially overlapped packages are heat-sealed, either it is not possible to get a seal of sufficient seal strength between the innermost heat-sealing layers

of each overlapped package or, if the temperature and pressure of the sealing bars are high enough to guarantee sealing through the overlapped webs, sealing of the overlapped outermost layers may occur, thus leading to a high number of rejects. This also means that in the packaging process the speed of the overall process is limited by the number of packages that, at each sealing cycle, can be positioned, without overlapping, in the vacuum and sealing chamber.

Using bags that can suitably be heat-sealed also when overlapping occurs, without problems of insufficient seal strength and/or sealing or sticking of the outer abuse layers, a higher number of packages could be sealed in each sealing cycle with an increase in productivity. Also, the positioning of the packages in the vacuum and sealing chamber, one along the other with no overlapping, would not be a must thus rendering the presence of an operator dedicated to said positioning, less critical.

While it is easy to list the desired properties, getting a suitable balance thereof by means of a stable and reproducible manufacturing process is not always possible.

## SUMMARY OF THE INVENTION

We have discovered films which can provide for a combination of desirable characteristics: high impact strength, high abuse resistance, high free shrink at 90 °C, high gloss and package presentation, good sealability and seal strength, and stack/overlap sealing capability and can be manufactured via a stable and controlled process.

In a first aspect, the present invention is directed to a heat-shrinkable multi-layer film comprising at least

- a first outer heat-sealing layer (a) comprising one or more polyolefins;
- a second outer abuse layer (b) comprising a polyamide with melting point  $\geq 175$  °C; and
- an intermediate gas barrier layer (c) comprising PVDC.

In a second aspect the present invention is directed to a heat-shrinkable multi-layer film comprising at least

- a first outer heat-sealing layer (a) comprising one or more polyolefins;
- a second outer abuse layer (b) comprising a polyamide with melting point  $\geq 175$  °C; and

an intermediate gas barrier layer (c) comprising PVDC,  
in the form of a seamless tube with outer heat-sealing layer (a) being the innermost layer  
of the tube.

5 In a third aspect the present invention is directed to a container obtained from a heat-shrinkable multi-layer film comprising at least

a first outer heat-sealing layer (a) comprising one or more polyolefins;  
a second outer abuse layer (b) comprising a polyamide with melting point  $\geq 175$  °C; and  
an intermediate gas barrier layer (c) comprising PVDC,  
by a welding that involves the heat-sealing outer layer (a).

10 In a fourth aspect the present invention is directed to a process of manufacture of a heat-shrinkable multi-layer film comprising at least

a first outer heat-sealing layer (a) comprising one or more polyolefins;  
a second outer abuse layer (b) comprising a polyamide with melting point  $\geq 175$  °C; and  
an intermediate gas barrier layer (c) comprising PVDC,

15 that comprises (co)-extrusion of at least the first outer heat-sealing layer (a) and possibly  
of other but not all the layers of the overall structure in the desired sequence, to give a first  
extrudate; extrusion coating of the obtained first extrudate with the remaining layers of the  
overall structure in the desired sequence, to give a second extrudate; and orientation thereof.

#### DEFINITIONS

20 In this specification and the accompanying claims:

the term "film" refers to a flat or tubular flexible structure of thermoplastic material having  
a thickness up to about 150  $\mu\text{m}$ ;

the term "heat-shrinkable" refers to a film that shrinks by at least 10 % of its original  
dimensions, in at least one of the longitudinal and transverse directions, when heated to 90 °C  
25 for 4 seconds;

the phrase "longitudinal direction" or "machine direction", herein abbreviated "MD",  
refers to a direction "along the length" of the film, i.e., in the direction of the film as the film  
is formed during extrusion and/or coating;

the phrase "transverse direction", herein abbreviated "TD", refers to a direction across the film, perpendicular to the machine direction;

the phrase "outer layer" refers to any film layer having only one of its principal surfaces directly adhered to another layer of the film;

5 the phrases "sealing-layer", "heat-sealable layer" and "heat sealing layer", refer to the outer film layer involved in the sealing of the film to itself, to another film, and/or to another article which is not a film;

the phrase "abuse layer" and "abuse-resistant layer" refer to the outside layer of the film which is not the sealant layer and which is subject to abuse;

10 the phrases "inner layer", "intermediate layer", and "internal layer" refer to any film layer having both of its principal surfaces directly adhered to another layer of the film;

the phrase "tie layer" refers to any internal layer having the primary purpose of adhering two layers to one another;

15 the term "core", and the phrase "core layer" refer to any internal layer which preferably has a function other than serving as a tie or compatibilizer for adhering two layers to one another;

the phrase "directly adhered", as applied to film layers, is defined as adhesion of the subject film layer to the object film layer, without a tie layer, adhesive, or other layer there-between. In contrast, as used herein, the word "between", as applied to a film layer, expressed as being between two other specific layers, includes both direct adherence of the subject layer  
20 to the two other layers it is between, as well as a lack of direct adherence to either or both of the two other layers the subject layer is between, i.e., one or more additional layers can be imposed between the subject layer and one or more of the layers the subject layer is between.

As used herein, the term "homopolymer" is used with reference to a polymer resulting from the polymerization of a single monomer, i.e., a polymer consisting essentially of a single  
25 type of repeating unit.

As used herein, the term "copolymer" refers to polymers formed by the polymerization reaction of at least two different monomers.

As used herein, the term "polymer" refers to both homo-polymers and co-polymers as defined above.

As used herein the term "polyolefin" is used with reference to any thermoplastic polymer of simple olefins such as ethylene, propylene, and butene, and co-polymer comprising a major proportion of a simple olefin and a minor proportion of one or more comonomers copolymerisable therewith such as typically another olefin, vinyl acetate, alkyl (meth)acrylate, (meth)acrylic acid, maleic anhydride, and the like, as well as modifications thereof. The term "polyolefin" specifically includes polyethylene, ethylene co-and ter-polymers, polybutene, propylene-butene co-polymer, and the like.

As used herein the terms "polyethylene" and "ethylene homopolymer" identify polymers consisting essentially of an ethylene repeating unit. Depending on the polymerization process employed, polymers with a different degree of branching and a different density can be obtained. Those characterized by a low degree of branching and showing a density higher than 0.940 g/cm<sup>3</sup> are called HDPE while those with a higher level of branching and a density up to 0.940 g/cm<sup>3</sup> are called LDPE.

As used herein the term "ethylene copolymer" refers to the copolymers of ethylene with one or more other olefins and/or with a non-olefinic comonomer copolymerizable with ethylene, such as vinyl monomers, modified polymers thereof, and the like. Specific examples include ethylene/ $\alpha$ -olefin copolymers, ethylene/vinyl acetate copolymers, ethylene/ethyl acrylate copolymers, ethylene/butyl acrylate copolymers, ethylene/methyl acrylate copolymers, ethylene/acrylic acid copolymers, ethylene/methacrylic acid copolymers, ionomer resins, ethylene/alkyl acrylate/maleic anhydride ter-polymers, etc..

As used herein, the phrase "heterogeneous polymer" refers to polymerization reaction products of relatively wide variation in molecular weight and relatively wide variation in composition distribution, i.e., polymers made, for example, using conventional Ziegler-Natta catalysts. Such polymers typically contain a relatively wide variety of chain lengths and comonomer percentages.

As used herein, the phrase "homogeneous polymer" refers to polymerization reaction products of relatively narrow molecular weight distribution and relatively narrow composition distribution. Homogeneous polymers exhibit a relatively even sequencing of comonomers within a chain, the mirroring of sequence distribution in all chains, and the similarity of length of all chains, and are typically prepared using metallocene, or other single-site type catalysis.

More particularly, homogeneous ethylene/ $\alpha$ -olefin copolymers may be characterized by one or more methods known to those of skill in the art, such as molecular weight distribution (Mw/Mn), composition distribution breadth index (CDBI), and narrow melting point range and single melt point behavior.

A homogeneous ethylene/ $\alpha$ -olefin copolymer can, in general, be prepared by the copolymerization of ethylene and any one or more  $\alpha$ -olefin. Preferably, the  $\alpha$ -olefin is a C<sub>3</sub>-C<sub>20</sub>  $\alpha$ -mono-olefin, more preferably, a C<sub>4</sub>-C<sub>12</sub>  $\alpha$ -mono-olefin, still more preferably, a C<sub>4</sub>-C<sub>8</sub>  $\alpha$ -mono-olefin. Still more preferably, the  $\alpha$ -olefin comprises at least one member selected from the group consisting of butene-1, hexene-1, and octene-1. Most preferably, the  $\alpha$ -olefin comprises octene-1, and/or a blend of hexene-1 and butene-1.

Processes for preparing homogeneous polymers are disclosed in US Patent No. 5,206,075, US Patent No. 5,241,031, and PCT International Application WO 93/03093. Further details regarding the production and use of one genus of homogeneous ethylene/ $\alpha$ -olefin copolymers are disclosed in US Patent No. 5,206,075, to Hodgson, Jr.; US Patent No. 5,241,031, to Mehta; PCT International Publication Number WO 93/03093, in the name of Exxon Chemical Company; and PCT International Publication Number WO 90/03414, in the name of Exxon Chemical Patents, Inc.. Still another genus of homogeneous ethylene/ $\alpha$ -olefin copolymers is disclosed in US Patent No. 5,272,236, to Lai, et.al., and US Patent No. 5,278,272, to Lai, et.al..

As used herein, the phrase "ethylene/ $\alpha$ -olefin copolymers", "ethylene/ $\alpha$ -olefin copolymers", refer to such heterogeneous materials as linear low density polyethylene (LLDPE), linear medium density polyethylene (LMDPE) and very low and ultra low density polyethylene (VLDPE and ULDPE); and homogeneous polymers such as metallocene

catalyzed polymers such as EXACT™ materials supplied by Exxon, AFFINITY™ and ENGAGE™ materials supplied by Dow, LUFLEXEN™ materials supplied by BASF and TAFMER™ materials supplied by Mitsui Petrochemical Corporation. These materials generally include copolymers of ethylene with one or more comonomers selected from C4 to C10  $\alpha$ -olefins such as butene-1, hexene-1, octene-1, etc..

As used herein the term "modified polyolefin" is inclusive of modified polymer prepared by copolymerizing the homopolymer of the olefin or copolymer thereof with an unsaturated carboxylic acid, e.g., maleic acid, fumaric acid or the like, or a derivative thereof such as the anhydride, ester or metal salt or the like; as well as of modified polymer obtained by incorporating, into the olefin homopolymer or copolymer, an unsaturated carboxylic acid, e.g. maleic acid, fumaric acid, or the like, or a derivative thereof such as the anhydride, ester or metal salt or the like. Examples of said modified polyolefins are graft copolymers of maleic acid or anhydride onto ethylene/ $\alpha$ -olefin copolymers, graft copolymers of fused ring carboxylic anhydrides onto polyethylene, resin mixtures of these and mixtures with polyethylene or ethylene/ $\alpha$ -olefin copolymers.

As used herein the term "ethylene-acrylic acid and ethylene-methacrylic acid copolymers" refers to copolymers of ethylene with a copolymerisable ethylenically unsaturated carboxylic acidic monomer selected from acrylic acid and methacrylic acid. The copolymer typically contains from about 4 to about 18% by weight of acrylic or methacrylic acid units. Said copolymer can also contain, copolymerised therein an alkyl (meth)acrylate, such as n-butyl acrylate or methacrylate or isobutyl acrylate or methacrylate. Said copolymer can be in the free acid form as well as in the ionized or partially ionized form wherein the neutralizing cation can be any suitable metal ion, e.g. an alkali metal ion, a zinc ion or other multivalent metal ions; in this latter case the copolymer is also termed "ionomer".

As used herein the term "ethylene-vinyl acetate copolymer" or "EVA" is intended to refer to a copolymer formed from ethylene and vinyl acetate monomers wherein the ethylene derived units in the copolymer are present in major amounts; preferably between about 60 %

and 98 % by weight and the vinyl acetate derived units in the copolymer are present in minor amounts, preferably between about 2 % and about 40 % by weight.

As used herein the term "ethylene-alkyl (meth)acrylate copolymers" refers to copolymers of ethylene with alkyl (meth)acrylates, e.g. methyl (meth)acrylate, butyl (meth)acrylate, and iso-butyl (meth)acrylate wherein the ethylene derived units in the copolymer are present in major amounts and the alkyl (meth)acrylate derived units in the copolymer are present in minor amounts, preferably between about 2 % and about 28 % by weight.

As used herein the term EVOH refers to saponified products of ethylene-vinyl ester copolymers, generally of ethylene-vinyl acetate copolymers, wherein the ethylene content is typically comprised between 20 and 60 % by mole and the degree of saponification is generally higher than 85 % preferably higher than 95 %.

As used herein the term PVDC refers to a vinylidene chloride copolymer wherein a major amount of the copolymer comprises vinylidene chloride and a minor amount of the copolymer comprises one or more unsaturated monomers copolymerisable therewith, typically vinyl chloride, and alkyl acrylates or methacrylates (e.g. methyl acrylate or methacrylate) or to a blend thereof in different proportions. Generally said PVDC contains plasticisers and/or stabilizers as known in the art.

As used herein, the term polyamide is intended to refer to both polyamides and copolyamides. This term specifically includes those aliphatic polyamides or copolyamides commonly referred to as e.g. polyamide 6 (homopolymer based on  $\epsilon$ -caprolactam), polyamide 69 (homopolycondensate based on hexamethylene diamine and azelaic acid), polyamide 610 (homopolycondensate based on hexamethylene diamine and sebacic acid), polyamide 612 (homopolycondensate based on hexamethylene diamine and dodecandioic acid), polyamide 11 (homopolymer based on 11-aminoundecanoic acid), polyamide 12 (homopolymer based on  $\omega$ -aminododecanoic acid or on laurilactam), polyamide 6/12 (polyamide copolymer based on  $\epsilon$ -caprolactam and laurilactam), polyamide 6/66 (polyamide copolymer based on  $\epsilon$ -caprolactam and hexamethylenediamine and adipic acid), polyamide 66/610 (polyamide copolymers based on hexamethylenediamine, adipic acid and sebacic



acid), modifications thereof and blends thereof. Said term also includes crystalline or partially crystalline, aromatic or partially aromatic, polyamides.

Melting information by DSC are reported as second heating data, i.e., the sample is heated at a programmed rate of 10 °C/min to a temperature below its critical range, cooled down and then reheated (2<sup>nd</sup> heating) still at a programmed rate of 10 °C/min.

#### DETAILED DESCRIPTION OF THE INVENTION

A first object of the present invention is a heat-shrinkable film comprising at least the following layers:

a first outer heat-sealing layer (a) comprising one or more polyolefins;

a second outer abuse layer (b) comprising a polyamide with melting point  $\geq 175$  °C; and

an intermediate gas barrier layer (c) comprising PVDC.

In the film according to the present invention the heat-sealing layer (a) may comprise a single polymer or a blend of two or more polymers as known in the art. Preferably the melting point of the polyolefin resin(s) of the heat-sealing layer (a) will be  $< 140$  °C, and preferably  $< 130$  °C. In a more preferred embodiment it will be comprised between about 80°C and about 128 °C.

Such a layer may for example comprise heterogeneous or homogeneous ethylene- ( $C_4$ - $C_8$ )- $\alpha$ -olefin copolymers having a density  $\leq 0.915$  g/cm<sup>3</sup>; blends thereof with minor amount of polyethylene homopolymers; ethylene-vinyl acetate copolymers; ethylene-acrylic or methacrylic acid copolymers including ionomers; blends of heterogeneous or homogeneous ethylene- ( $C_4$ - $C_8$ )- $\alpha$ -olefin copolymers having a density from about 0.915 g/cm<sup>3</sup> to about 0.930 g/cm<sup>3</sup> with ethylene-vinyl acetate copolymers or ethylene-alkyl (meth)acrylate copolymers; ethylene-propylene-butene ter-polymers; ethylene-alkyl acrylate-maleic anhydride ter-polymers; and the like polymers.

In a preferred embodiment of the present invention the heat-sealing layer (a) will comprise a heterogeneous or homogeneous ethylene- ( $C_4$ - $C_8$ )- $\alpha$ -olefin copolymer having a density  $\leq 0.915$  g/cm<sup>3</sup>, and even more preferably a heterogeneous or homogeneous ethylene- ( $C_4$ - $C_8$ )- $\alpha$ -olefin copolymer having a density comprised between about 0.895 g/cm<sup>3</sup> and about 0.912

g/cm<sup>3</sup>. The Melt Index of said heterogeneous or homogeneous ethylene-(C<sub>4</sub>-C<sub>8</sub>)- $\alpha$ -olefin copolymer may range from about 0.1 to about 15 g/10' (measured by ASTM D-1238, Condition E). However, preferred values are in the range 0.5-10 g/10' and still more preferred values are in the range 1.0-7.0 g/10'.

5 The resins used in the manufacture of the films according to the present invention, not only in the heat-sealing (a) but also in the outer abuse layer (b) or in any of the intermediate layers, can be suitably additivated as known in the art in order to improve the properties of the film or the manufacturing process thereof.

As an example the resins may contain stabilizers, anti oxidants, pigments, UV absorbers,  
10 cross-linking enhancers or cross-linking inhibitors, anti-fog agents, slip and anti-blocking agents, etc., as conventionally used in this field.

The polyamide of the outer layer (b) will have a melting point  $\geq 175$  °C, typically of from about 175 °C to about 250°C; preferably of from about 180 °C to about 240 °C; more preferably of from about 185 °C to about 230 °C; and still more preferably of from about 188  
15 °C to about 225 °C.

A most preferred group of polyamides, with a melting temperature of from about 188 °C to about 225 °C, suitable for use in the outer abuse layer (b), includes certain copolyamides 6/12, such as PA6/12 CR-8 and CR-9 marketed by EMS, polyamide 66, copolyamides 6/66 such as CA95WP marketed by Allied Signal, certain polyamide 6 copolymers (modified  
20 polyamide 6) comprising less than 5 %, preferably less than 4 %, and even more preferably less than 3 % by weight of an aromatic co-monomer such as terephthalic acid, such as Sniamid™ F36T/S marketed by Caffaro, certain copolyamides of polyamide 6 and a partially aromatic polyamide, such as Durethan™ CI31F and CI31FKS marketed by Bayer, and certain terpolyamides such as those based on polyamide 6, polyamide 11, and polyamide 66, sold by  
25 Bayer under the trade name Durethan™ VP KU 2-2153 or KU 2-2153F.

Preferably the outer abuse layer (b) will comprise polyamide 6, a modified polyamide 6, a co-polyamide of polyamide 6 and a partially aromatic polyamide, or a ter-polyamide based on polyamide 6, polyamide 11, and polyamide 66.

The outer abuse layer (b) will contain at least 50 % by weight and preferably at least 60 % by weight of one or more polyamides with a m.p.  $\geq 175$  °C.

In a preferred embodiment of the present invention the outer abuse layer (b) will comprise a blend comprising a polyamide having a m.p.  $\geq 175$  °C and an ethylene-vinyl alcohol copolymer. Preferred EVOH copolymers for use in such a blend will contain between about 30 and about 50 % by mole of ethylene.

When a blend with EVOH is employed for the outer abuse layer (b), the amount by weight of EVOH in said outer layer will be up to about 40 % with respect to the overall weight of the layer. Typically the amount of EVOH will be comprised between about 3 and about 40 % by weight, preferably between about 5 and about 35 % by weight, and even more preferably between about 10 and about 30 % by weight.

It has been found in fact that the presence of an amount of at least about 3 % by weight of EVOH in said outer abuse layer (b) improves stretchability of the tape, thus facilitating the orientation step and increasing the free shrink of the end structure, while it has also been found that the good mechanical properties and the stack/overlap sealing capability of the end film are maintained even when amounts as high as about 40 % by weight of EVOH are employed in said outer abuse layer (b).

The film according to the present invention requires the presence of an intermediate gas barrier layer (c) wherein said gas (e.g. oxygen, nitrogen, carbon dioxide, etc.) barrier layer comprises PVDC.

In an even more preferred embodiment the PVDC comprises vinylidene chloride-methyl acrylate copolymer, or vinylidene chloride-methyl methacrylate copolymer, or a blend of vinylidene chloride-vinyl chloride copolymer and a minor proportion of vinylidene chloride-methyl acrylate copolymer.

The thickness of the intermediate gas barrier layer (c) will generally be comprised between about 2 and about 15  $\mu\text{m}$ , as thicker gas barrier layers will not bring about any appreciable increase in barrier properties worth the additional costs involved, while thinner gas barrier layers cannot guarantee the desired low level of gas permeability. Preferably the

thickness of the intermediate gas barrier layer (c) will be comprised between about 3 and about 12  $\mu\text{m}$ , and even more preferably between about 4 and about 10  $\mu\text{m}$ .

The thickness of the outer abuse layer (b) will be typically comprised between about 2 and about 15  $\mu\text{m}$ , whereas a preferred thickness will be comprised between about 3 and about 10  $\mu\text{m}$ , and an even more preferred thickness will be comprised between about 4 and about 8  $\mu\text{m}$ . The outer abuse layer (b) needs in fact to be thick enough to provide for the desired good mechanical properties and the stack/overlap sealability, while it should not be too thick as otherwise stretchability of the tape and, as a consequence thereof, free shrink of the end structure, will be negatively affected.

The thickness of the outer heat-sealing layer (a) typically depends on the overall thickness of the film and on the number of layers present in the end structure. In case of thin films it generally ranges from about 2  $\mu\text{m}$  to e.g. about 6, or 8, or 10  $\mu\text{m}$ . In case of thicker films, such as those used for the manufacture of bags or pouches, it is typically greater than 4  $\mu\text{m}$ , preferably greater than 5  $\mu\text{m}$ , and even more preferably greater than 6  $\mu\text{m}$ , and up to about 20, 30, 40  $\mu\text{m}$  or even more.

Generally, the film has a total thickness of from about 12 to about 150  $\mu\text{m}$ ; preferably, from about 15 to about 130  $\mu\text{m}$ ; more preferably, from about 20 to about 120  $\mu\text{m}$ ; still more preferably, from about 30 to about 100  $\mu\text{m}$ ; yet still more preferably, from about 35 to about 90  $\mu\text{m}$ .

Additional inner layers can be added e.g. to increase the bulk of the overall structure and/or further improve the shrink and/or the mechanical properties of the film, etc. as known in the art.

Suitable resins for said additional intermediate layers include for instance ethylene copolymers, particularly ethylene-vinyl acetate copolymers, ethylene-alkyl acrylate or ethylene-alkyl methacrylate copolymers, ionomers, ethylene- $\alpha$ -olefin copolymers with a low density or very low density, and the like resins.

To improve the adhesion between the gas barrier layer (c) and the outer layers (a) and (b), or between the different layers, in case additional inner layers are present, tie layers can be

employed. Tie layers typically comprise a modified polyolefin or preferably a blend of a modified polyolefin with a polyolefin, such as for instance a blend of an acid or anhydride modified EVA with EVA or LLDPE. Their thickness is typically of few  $\mu\text{m}$  as their aim is just to increase the bond between the different layers.

5 In one embodiment of the present invention the film has at least four layers wherein a tie layer (d) is adhered to one of the surfaces of the gas barrier intermediate layer (c), and to either one of the outer abuse layer (c) and the outer heat-sealing layer (a). In particular, in the case of a four layer film, a tie layer (d) is generally required for bonding layer (c) to the outer abuse layer (b), while a direct adhesion between said PVDC comprising gas barrier layer (c) and the heat-sealing layer (a) may be achieved by suitably selecting the resin or the resin  
10 blend of the heat-sealing layer (a). As an example, direct adhesion between the PVDC comprising gas barrier layer (c) and the heat-sealing layer (a) can be obtained using, for the heat-sealing layer (a), ethylene-vinyl acetate copolymers, ethylene-alkyl acrylate copolymers, ethylene-alkyl methacrylate copolymers, ethylene- $\alpha$ -olefin copolymers, and the like polymers  
15 and blends thereof.

In another embodiment the film has at least five layers wherein a tie layer (d) is between the sealing layer (a) and one of the surfaces of the intermediate gas barrier layer (c), and another tie layer (d'), that may be equal to or different from (d) is between the other surface of the intermediate gas-barrier layer (c) and the outer abuse layer (b).

20 The films according to the present invention can be manufactured by the so-called trapped-bubble process, which is a widely known process typically used for the manufacture of the heat-shrinkable films for food contact packaging.

According to said process, the multi-layer film is co-extruded through a round die to obtain a tube of molten polymer which is quenched immediately after extrusion without being  
25 expanded, then heated to a temperature which is above the  $T_g$  of all the resins employed and below the melting temperature of at least one of said resins, typically by passing it through a hot water bath, but alternatively using a hot air tunnel or an I.R. oven, and expanded, still at this temperature by internal air pressure to get the transversal orientation and by a differential

speed of the pinch rolls which hold the thus obtained "trapped bubble" to provide the longitudinal orientation. The film is then rapidly cooled to somehow freeze the molecules of the film in their oriented state and wound.

While in a preferred embodiment of the present invention the film is biaxially oriented and will therefore be heat-shrinkable in both directions, mono-oriented films or preferentially oriented films can be obtained by avoiding or controlling transversal or longitudinal orientation. Suitable orientation ratios are typically comprised between 2 : 1 and 5 : 1, and are preferably comprised between 2.5 : 1 and 4 : 1. Higher orientation ratios can be applied when different technologies (e.g. tenter frame) are employed for the orientation or in case of mono-axially oriented films.

As used herein, the phrase "free shrink" refers to the percent dimensional change in a 10 cm x 10 cm specimen of film, when subjected to selected heat (i.e., at a certain temperature), with the quantitative determination being carried out according to ASTM D 2732, as set forth in the 1990 Annual Book of ASTM Standards, Vol. 08.02, pp.368-371, which is hereby incorporated, in its entirety, by reference thereto.

The multi-layer film according to the present invention typically has a total free shrink of at least 20 % at 90 °C, preferably of at least 30 % at 90 °C, more preferably of at least 40 % at 90 °C and even more preferably of at least 50 % at 90 °C. "Total free shrink" is determined by summing the percent free shrink in the machine direction with the percentage of free shrink in the transverse direction. For example, a film that exhibits, at 90 °C, 20 % free shrink in the transverse direction and 20 % free shrink in the machine direction, has a "total free shrink" at 90 °C of 40 %. Unless specified otherwise, the phrase "free shrink", as used herein, refers to total free shrink.

Depending on the number of layers in the structure it may be advisable or necessary to split the co-extrusion step : in such a case a tube is first formed of a limited number of layers, with the heat-sealing layer (a) on the inside of the tube; this tube is quenched quickly and, before submitting it to the orientation step, it is extrusion-coated with the remaining layers, again

quenched quickly and then passed to the orientation. During the extrusion-coating step the tube is slightly inflated just to keep it in the form of a tube and avoid that it collapses.

The coating step can be simultaneous, by coextruding all the remaining layers altogether, so as to simultaneously adhere all of them, one over the other, to the quenched tube obtained  
5 in the first extrusion step, or this coating step can be repeated as many times as the layers which are to be added.

According to a preferred embodiment of the present invention the film is partially or wholly cross-linked. Cross-linking may be achieved either by irradiation or chemically. Preferably cross-linking is achieved by irradiation that involves submitting the film to a  
10 suitable radiation dosage of high-energy electrons, preferably using an electron accelerator, with the dosage level being determined by standard dosimetry methods. A suitable radiation dosage of high-energy electrons is in the range of up to about 120 kGy, more preferably from about 16 to about 100 kGy, and still more preferably from about 20 to about 90 kGy.

The radiation is not limited to electrons from an accelerator since any ionizing radiation  
15 may be used.

Irradiation is most preferably performed prior to orientation, on the extruded primary tape, but it could also be performed after orientation on the end film or during orientation.

If only some of the layers of the film need to be irradiated, the extrusion coating technique is used and the irradiation step is carried out on the primary tube or sheet, before extrusion  
20 coating and orientation.

In a preferred embodiment of the invention, the film is obtained by extrusion coating and only the primary tape, that will not comprise the PVDC layer, is irradiatively cross-linked.

Particularly when the whole film is cross-linked by irradiation, it may be advantageous to make use of cross-linking controlling agents which can be added to the different layers in  
25 different amounts to control the degree of cross-linking in each layer. Suitable cross-linking controlling agents are for instance those described in EP-A-333,294.

Alternatively, chemical cross-linking of the resins can be achieved by the addition of suitable cross-linking agents, e.g. peroxides, to the resins to be cross-linked.

It is also possible to combine chemical cross-linking and irradiation, as an example when the cross-linking agents added to the resins need some irradiation to trigger the cross-linking reaction.

The films according to the present invention may optionally be subjected to other types of energetic radiation treatments that may have different aims. As an example the outer abuse layer (b) of the film may be subjected to a corona discharge treatment to improve the print receptivity characteristics of the film surface or the outer heat-sealant layer (a) may be subjected to a corona discharge treatment to improve the heat-sealability and/or the meat adhesion properties thereof.

In some instances it may be desirable to submit the oriented structure to an annealing step; this typically consists in a controlled heating-cooling treatment that is carried out on the oriented film in order to have better control on low temperature dimensional stability of the heat-shrinkable film while maintaining the shrink properties at higher temperatures.

The film of the present invention may be used either as a film, or as a bag or pouch, or as a tubing to form a package in a conventional manner.

In a preferred embodiment the heat-shrinkable film of the present invention is obtained as a seamless tubular film wherein the heat-sealing layer (a) is the innermost layer of the tube and the outer abuse layer (b) is the outermost layer of the tube and, if desired, individual bags are formed by transverse sealing and cutting across the flattened tubular film.

In a second aspect, therefore, the present invention is directed to a heat-shrinkable multi-layer film comprising at least

a first outer heat-sealing layer (a) comprising one or more polyolefins;

a second outer abuse layer (b) comprising a polyamide with melting point  $\geq 175$  °C; and

an intermediate gas barrier layer (c) comprising PVDC,

in the form of a seamless tube with outer heat-sealing layer (a) being the innermost layer of the tube.

Alternatively the film may also be prepared by flat extrusion (co-extrusion or extrusion coating) followed by orientation in one or both directions via tenter frame. Orientation may be



carried out in such a case either sequentially or simultaneously. The flat film can then be converted to transverse sealed (TS) bags or pouches, by center-folding the film and then transversely sealing and severing it. Other methods of making bags and packages are known and may be readily adapted to use with the multi-layer films of the invention. Preferably, the bag is produced by sealing the outer heat-sealing layer (a) to itself, whereby said outer layer is an inside bag layer and the outer abuse layer (b) is an outside bag layer.

In a third aspect the present invention is directed to a container obtained from a heat-shrinkable multi-layer film comprising at least

a first outer heat-sealing layer (a) comprising one or more polyolefins;

a second outer abuse layer (b) comprising a polyamide with melting point  $\geq 175$  °C; and

an intermediate gas barrier layer (c) comprising PVDC,

by a welding involving the outer heat-sealing layer (a), whereby said outer layer (a) is the inside bag layer and the outer abuse layer (b) is the outside bag layer.

The present invention will now be described in more detail with particular reference to the following Examples:

#### Example 1

A seven-layer film has been prepared by extrusion coating through a round die.

A substrate formed of the following layers (a)/(e)/(f)/(g), wherein the heat-sealing layer (a) is the innermost layer of the tube, has been co-extruded, quickly quenched with a water cascade, irradiated at a dosage level of 64 kGy and coated with the sequence of three layers, (c)/(d)/(b), wherein the outer abuse layer (b) is the outermost layer of the overall tube. The extrusion coated tape has then been quenched, re-heated by passing it through a water bath at about 95 °C-98 °C, and oriented at this temperature (with orientation ratios of about 3.6 : 1 in the longitudinal direction and about 3.2 : 1 in the transverse direction) by the trapped-bubble process.

The sequence of layers (from the innermost heat-sealing layer (a) to the outermost abuse layer (b)) in the overall structure is as follows:

(a)/(e)/(f)/(g)/(c)/(d)/(b)

wherein the resins used for the different layers and, between parentheses, the thickness of each layer are reported below:

(a) homogeneous ethylene-octene-1 copolymer -  $d = 0.905 \text{ g/cm}^3$  - m.p. =  $99^\circ\text{C}$  (DSC - 2<sup>nd</sup> heating) - MI = 6 g/10' (measured by ASTM D1238 - Condition E ( $190^\circ\text{C}$ , 2.16 kg)) - Affinity PL 1280 by Dow (9  $\mu\text{m}$ )

(e) a blend of 70 % by weight of ethylene-vinyl acetate copolymer [14 % VA, MI = 0.25 g/10' (measured by ASTM D1238 - Condition E ( $190^\circ\text{C}$ , 2.16 kg)) – Escorene Ultra FI00014 by Exxon] and 30 % by weight of heterogeneous ethylene-octene-1 copolymer [ $d = 0.920 \text{ g/cm}^3$  - m.p. =  $124^\circ\text{C}$  (DSC - 2<sup>nd</sup> heating) - MI = 1 g/10' (measured by ASTM D1238 - Condition E ( $190^\circ\text{C}$ , 2.16 kg)) – Dowlex 2045 E by Dow] (6  $\mu\text{m}$ )

(f) a blend of 20 % by weight of ethylene-vinyl acetate copolymer [14 % VA, MI = 0.25 g/10' (measured by ASTM D1238 - Condition E ( $190^\circ\text{C}$ , 2.16 kg)) – Escorene Ultra FI00014 by Exxon] and 80 % by weight of heterogeneous ethylene-octene-1 copolymer [ $d = 0.920 \text{ g/cm}^3$  - m.p. =  $124^\circ\text{C}$  (DSC - 2<sup>nd</sup> heating) - MI = 1 g/10' (measured by ASTM D1238 - Condition E ( $190^\circ\text{C}$ , 2.16 kg)) – Dowlex 2045 E by Dow] (7  $\mu\text{m}$ )

(g) a blend of 70 % by weight of ethylene-vinyl acetate copolymer [14 % VA, MI = 0.25 g/10' (measured by ASTM D1238 - Condition E ( $190^\circ\text{C}$ , 2.16 kg)) – Escorene Ultra FI00014 by Exxon] and 30 % by weight of heterogeneous ethylene-octene-1 copolymer [ $d = 0.920 \text{ g/cm}^3$  - m.p. =  $124^\circ\text{C}$  (DSC - 2<sup>nd</sup> heating) - MI = 1 g/10' (measured by ASTM D1238 - Condition E ( $190^\circ\text{C}$ , 2.16 kg)) – Dowlex 2045 E by Dow] (8  $\mu\text{m}$ )

(c) a blend of 30 % by weight of vinylidene chloride-methyl acrylate copolymer, 68 % by weight of vinylidene chloride-vinyl chloride and 2 % by weight of epoxidised soybean oil (6  $\mu\text{m}$ )

(d) anhydride grafted and rubber modified LLDPE - Tymor 1203 by Morton (4  $\mu\text{m}$ )

(b) a blend of 30 % by weight of EVOH [(44 mole % ethylene) - EVAL EP-105A by Marubeni] and 70 % by weight of a terpolyamide based on polyamide 6, polyamide 11, and polyamide 66 [sold by Bayer under the trade name Durethan® VP KU 2-2153 (m.p.  $191^\circ\text{C}$ )] (6  $\mu\text{m}$ ).

### Example 2

A seven layer film has been obtained by following substantially the same procedure described in the foregoing example but replacing the resins used for layers (e), (f), and (g), with the following ones :

5 (e') ethylene-vinyl acetate copolymer [14 % VA, MI = 0.25 g/10' (measured by ASTM D1238 - Condition E (190 °C, 2.16 kg)) – Escorene Ultra FI00014 by Exxon]

(f') ethylene-methacrylic acid copolymer [12 % MA, MI = 1.6 g/10' (measured by ASTM D1238 - Condition E (190 °C, 2.16 kg)) – Nucrel 1202 by DuPont]

10 (g') ethylene-vinyl acetate copolymer [14 % VA, MI = 0.25 g/10' (measured by ASTM D1238 - Condition E (190 °C, 2.16 kg)) – Escorene Ultra FI00014 by Exxon]

### Example 3

A seven-layer film has been obtained by following substantially the same procedure described in Example 1 but replacing the blend used in layer (b) with the following one :

15 (b') blend of 15 % by weight of EVOH [(44 mole % ethylene) - EVAL EP-105A by Marubeni] and 85 % by weight of a polyamide 6/66 with m.p. 196 °C [marketed by Allied Signal as CA95WP].

### Example 4

A five-layer film has been prepared by extrusion coating through a round die.

20 A substrate formed of the following two layers (a')/(e''), wherein the heat-sealing layer (a) is the innermost layer of the tube, has been co-extruded, quickly quenched with a water cascade, irradiated at a dosage level of 64 kGy and coated with the sequence of three layers, (c)/(d)/(b), wherein the outer abuse layer (b) is the outermost layer of the overall tube. The extrusion-coated tape has then been quenched, re-heated by passing it through a water bath at about 95 °C-98 °C, and oriented at this temperature by the trapped-bubble process.

25 The sequence of layers (from the innermost heat-sealing layer (a) to the outermost abuse layer (b)) in the overall structure is as follows:

(a')/(e'')/(c)/(d)/(b)

wherein the resins used for the layers and, between parentheses, the thickness of each layer are reported below:

(a') heterogeneous ethylene-octene-1 copolymer [ $d = 0.911 \text{ g/cm}^3$  -  $MI = 7 \text{ g/10'}$  (measured by ASTM D1238 - Condition E (190 °C, 2.16 kg)) - Stamylex 08-076 by DSM]  
5 (14  $\mu\text{m}$ )

(e'') ethylene-vinyl acetate copolymer [9 % VA,  $MI = 3.0 \text{ g/10'}$  (measured by ASTM D1238 - Condition E (190 °C, 2.16 kg)) - Evatane 1020 VN 3 by Elf Atochem] (20  $\mu\text{m}$ )

(c), (d), and (b) have the same composition as in Example 1 and a thickness of about 5  $\mu\text{m}$  each.

#### 10 Example 5

A five layer film has been prepared by following essentially the same procedure as in the foregoing Example 4 but replacing in the outermost layer the blend (b) with the blend (b') described in Example 3.

#### Example 6

15 A seven layer film has been obtained by following substantially the same procedure as in Example 2 but replacing in the outermost layer the blend (b) with the blend (b') described in Example 3 and modifying the thickness of the layers.

In the overall structure (a)/(e'')/(f'')/(g'')/(c)/(d)/(b') the thickness of each layer is, expressed in  $\mu\text{m}$ , 13/6/6/7//5/9/3.

#### 20 Example 7

A five-layer film has been prepared by following substantially the same procedure described in Example 4 but replacing the blend used in the outermost layer with the following one :

(b'') blend of 25 % by weight of EVOH [(44 mole % ethylene) - EVAL EP-105A by Marubeni] and 75 % by weight of polyamide 6 copolymer (polycaprolactam containing about  
25 1 % terephthalic acid comonomer) with m.p. = 213°C (DSC - 2<sup>nd</sup> heating) - [Sniamid F36T/S by Caffaro].

#### Example 8

A five-layer film has been prepared essentially as described in Example 4 but replacing the blend used for the outer abuse layer (b) with

(b''') blend of 10 % by weight of EVOH [(44 mole % ethylene) - EVAL EP-105A by Marubeni] and 90 % by weight of co-polyamide 6/6I with m.p. = 188-190 °C (DSC - 2<sup>nd</sup> heating) [Durethan™ CI31F by Bayer].

#### Examples 9 and 10

Two seven layer films have been prepared essentially as described in Example 1 but adding to the blend used for the outer abuse layer (b), 4 wt. % of a masterbatch of slip and antiblocking agents in a polyamide 6/12 copolymer with m.p. ≈ 190 °C (Grilon 3476FS by ESM - Example 9) or in a polyamide 6/12 copolymer with m.p. ≈ 135 °C (Grilon 7361FS by EMS - Example 10).

#### Example 11

A seven-layer film is prepared essentially as described in Example 1 but replacing the blend used for the outer abuse layer (b) with

(b<sup>iv</sup>) a ternary copolyamide based on polyamide 6, polyamide 11, and polyamide 66 with m.p. = 191 °C (DSC- 2<sup>nd</sup> heating) - [Durethan™ VP KU 2-2153 by Bayer].

#### Example 12

A seven-layer film is prepared essentially as described in Example 1 but replacing the blend used for the outer abuse layer (b) with

(b<sup>v</sup>) a co-polyamide 6/12 with m.p. = 190 °C ((DSC- 2<sup>nd</sup> heating) [CR-8 by EMS].

#### Example 13

A seven-layer film is prepared essentially as described in Example 1 but replacing the blend used for the outer abuse layer (b) with

(b<sup>vi</sup>) a blend of 30 % by weight of EVOH [(44 mole % ethylene) - EVAL EP-105A by Marubeni] and 70 % by weight of a co-polyamide 6/12 with m.p. = 190 °C ((DSC- 2<sup>nd</sup> heating) [CR-8 by EMS].

#### Example 14

A seven-layer film is prepared essentially as described in Example 1 but replacing the resin used for layer (d) with

(d') a modified VLDPE resin sold by Mitsui as Admer AT 1094E.

#### Example 15

A seven-layer film is prepared essentially as described in Example 1 but replacing the blend used for the outer abuse layer (b) with

(b<sup>vii</sup>) a blend of 30 % by weight of EVOH [(44 mole % ethylene) - EVAL EP-105A by Marubeni] and 70 % by weight of co-polyamide 6/6I with m.p. = 188-190 °C (DSC - 2<sup>nd</sup> heating) [Durethan™ CI31F by Bayer].

#### Example 16

A seven-layer film is prepared by following essentially the same procedure of Example 1.

A substrate formed of the following layers (a')/(e')/(f')/(g'), wherein the heat-sealing layer (a') is the innermost layer of the tube, has been co-extruded, quickly quenched with a water cascade, irradiated at a dosage level of 64 kGy and coated with the sequence of three layers, (c)/(d')/(b<sup>iv</sup>), wherein the outer abuse layer (b<sup>iv</sup>) is the outermost layer of the overall tube. The extrusion coated tape has then been quenched, re-heated by passing it through a water bath at about 95 °C-98 °C, and oriented at this temperature (with orientation ratios of about 3.6 : 1 in the longitudinal direction and about 3.2 : 1 in the transverse direction) by the trapped-bubble process.

The sequence of layers (from the innermost heat-sealing layer (a') to the outermost abuse layer (b<sup>iv</sup>) in the overall structure is as follows:

(a')/(e')/(f')/(g')/(c)/(d')/(b<sup>iv</sup>)

wherein the resins used for the different layers and, between parentheses, the thickness of each layer are reported below:

(a') heterogeneous ethylene-octene-1 copolymer [ $d = 0.911 \text{ g/cm}^3$  -  $MI = 7 \text{ g/10'}$  (measured by ASTM D1238 - Condition E (190 °C, 2.16 kg)) - Stamylex 08-076 by DSM] (11  $\mu\text{m}$ )

(e') ethylene-vinyl acetate copolymer [14 % VA, MI = 0.25 g/10' (measured by ASTM D1238 - Condition E (190 °C, 2.16 kg)) – Escorene Ultra FI00014 by Exxon] (6 µm)

(f') ethylene-methacrylic acid copolymer [12 % MA, MI = 1.6 g/10' (measured by ASTM D1238 - Condition E (190 °C, 2.16 kg)) – Nucrel 1202 by DuPont] (6 µm)

5 (g') ethylene-vinyl acetate copolymer [14 % VA, MI = 0.25 g/10' (measured by ASTM D1238 - Condition E (190 °C, 2.16 kg)) – Escorene Ultra FI00014 by Exxon] (6 µm)

(c) a blend of 30 % by weight of vinylidene chloride-methyl acrylate copolymer, 68 % by weight of vinylidene chloride-vinyl chloride and 2 % by weight of epoxidised soybean oil (6 µm)

10 (d') modified VLDPE – Admer AT 1094 E by Mitsui (4 µm)

(b<sup>iv</sup>) a terpolyamide based on polyamide 6, polyamide 11, and polyamide 66 [sold by Bayer under the trade name Durethan® VP KU 2-2153 (m.p. 191 °C)] (6 µm).

#### Example 17

A seven layer film is prepared essentially as described in Example 16 but replacing the  
15 resin used for layer (d') with

(d) anhydride grafted and rubber modified LLDPE - Tymor 1203 by Morton.

#### Example 18

A seven-layer film is prepared essentially as described in Example 11 but replacing the resin used for the heat-sealing layer (a) with the following resin

20 (a') heterogeneous ethylene-octene-1 copolymer [ $d = 0.911 \text{ g/cm}^3$  - MI = 7 g/10' (measured by ASTM D1238 - Condition E (190 °C, 2.16 kg)) – Stamylex 08-076 by DSM] and the resin (f) with the following one

(f') ethylene-methacrylic acid copolymer [12 % MA, MI = 1.6 g/10' (measured by ASTM D1238 - Condition E (190 °C, 2.16 kg)) – Nucrel 1202 by DuPont].

#### 25 Example 19

A seven layer film is prepared essentially as described in Example 11 but replacing the resin used for layer (d) with

(d') modified VLDPE – Admer AT 1094 E by Mitsui.

## Example 20

A seven-layer film is prepared essentially as described in Example 19 but replacing the resin used for the outer abuse layer (b<sup>iii</sup>) with

(b<sup>vi</sup>) a blend of 30 % by weight of EVOH [(44 mole % ethylene) - EVAL EP-105A by Marubeni] and 70 % by weight of a co-polyamide 6/12 with m.p. = 190 °C ((DSC- 2<sup>nd</sup> heating) [CR-8 by EMS].

## Example 21

A seven-layer film is prepared essentially as described in Example 19 but replacing the resin used for the outer abuse layer (b<sup>iii</sup>) with

(b<sup>viii</sup>) a blend of 30 % by weight of EVOH [(44 mole % ethylene) - EVAL EP-105A by Marubeni] and 70 % by weight of a co-polyamide 6/12 with m.p. = 199 °C ((DSC- 2<sup>nd</sup> heating) [CF-85 by EMS].

## Example 22

A seven-layer film is prepared essentially as described in Example 1 but replacing the resin used for the outer abuse layer (b) with

(b<sup>ix</sup>) a blend of 30 % by weight of EVOH [(44 mole % ethylene) - EVAL EP-105A by Marubeni] and 70 % by weight of a co-polyamide 6/66 with m.p. = 196 °C ((DSC- 2<sup>nd</sup> heating) [Ultramid C35 by BASF].

## Example 23

A seven layer film is prepared essentially as described in Example 6 but replacing the resin used for the outer abuse layer (b') with

(b<sup>ix</sup>) a blend of 30 % by weight of EVOH [(44 mole % ethylene) - EVAL EP-105A by Marubeni] and 70 % by weight of a co-polyamide 6/66 with m.p. = 196 °C ((DSC- 2<sup>nd</sup> heating) [Ultramid C35 by BASF], and the resin used for intermediate layer (f') with

(f'') heterogeneous ethylene-octene-1 copolymer [ $d = 0.920 \text{ g/cm}^3$  - m.p. = 124 °C (DSC - 2<sup>nd</sup> heating) - MI = 1 g/10' (measured by ASTM D1238 - Condition E (190 °C, 2.16 kg)) - Dowlex 2045 E by Dow].

## Example 24



A seven-layer film is prepared essentially as described in Example 16 but replacing the resin used for the outer abuse layer (b<sup>iv</sup>) with

(b<sup>ix</sup>) a blend of 30 % by weight of EVOH [(44 mole % ethylene) - EVAL EP-105A by Marubeni] and 70 % by weight of a terpolyamide based on polyamide 6, polyamide 11, and  
5 polyamide 66 [sold by Bayer under the trade name Durethan® VP KU 2-2153 (m.p. 191 °C)]

#### Example 25

A seven layer film is prepared essentially as described in Example 24 but replacing the resin used for layer (f') with

(f'') heterogeneous ethylene-octene-1 copolymer [ $d = 0.920 \text{ g/cm}^3$  - m.p. = 124 °C (DSC -  
10 2<sup>nd</sup> heating) - MI = 1 g/10' (measured by ASTM D1238 - Condition E (190 °C, 2.16 kg)) - Dowlex 2045 E by Dow].

#### Example 26

A seven-layer film is prepared essentially as described in Example 24 but replacing the resin used for the outer abuse layer (b<sup>ix</sup>) with

15 (b<sup>vii</sup>) a blend of 30 % by weight of EVOH [(44 mole % ethylene) - EVAL EP-105A by Marubeni] and 70 % by weight of co-polyamide 6/6I with m.p. = 188-190 °C (DSC - 2<sup>nd</sup> heating) [Durethan™ CI31F by Bayer].

#### Example 27

A seven-layer film is prepared by following exactly the same procedure described in  
20 Example 11 but avoiding the irradiation step.

#### Example 28

A seven-layer film is prepared by following exactly the same procedure described in Example 17 but reducing the dosage level of the irradiation step to 42 kGy.

#### Example 29

25 A five layer film is prepared by following the same procedure as in Example 5 but varying the thickness of the gas barrier layer (c) from about 5 µm to about 7 µm, and that of the outer abuse layer (b') from about 5 µm to about 3 µm.

The properties of representative examples of films according to the present invention have been evaluated by submitting the films to the tests indicated below.

% Free shrink : the percent free shrink, i.e. the irreversible and rapid reduction, as a percent, of the original dimensions of a sample subjected to a given temperature under conditions where nil restraint to inhibit shrinkage is present, has been measured according to ASTM D2732, by immersing for 4 seconds specimens of the structures to be tested (10 cm x 10 cm) into a bath of hot water at 90 °C. This attribute has been measured in the longitudinal direction (LD) as well as in the transversal direction (TD) and is reported as the sum thereof, i.e. the total free shrink.

Haze : haze is defined as that percentage of transmitted light which in passing through the specimen deviates from the incident beam by forward scattering, and it has been measured by ASTM D 1003 (Procedure A).

Gloss : the specular gloss of the films, i.e. the relative luminous reflectance factor of a specimen in the mirror direction has been measured using ASTM 2457 - 90 with a gloss angle of 60°.

Modulus : the ratio of the tensile stress to corresponding strain below the proportional limit ( $\text{kg/cm}^2$ ); measured by ASTM D 882.

Tensile : a measure of the force required at constant elongation to break a specimen of the film ( $\text{kg/cm}^2$ ); measured by ASTM D 882.

Elongation : a measure of the percent extension required to break a specimen of the film (%); measured by ASTM D 882.

Puncture resistance : the puncture resistance is the resistance force arising when pushing a punch against a surface of flexible film. There is not a standard test method to measure this attribute. The test method used in the present evaluations is described briefly herein below : a film sample (6.5 cm x 6.5 cm) is fixed in a specimen holder connected to a compression cell (1-50 kg normal sensitivity) mounted on a dynamometer (an Instron tensile tester); when the dynamometer is started, a punch (a punching sphere, 5-mm in diameter, soldered on a

plunger) is brought against the film sample at a constant speed (30 cm/min.) and the force needed to puncture the sample is graphically recorded.

In-line abuse resistance : the capability of the tested structures to withstand without breakage the in-line packaging operations, i.e. loading, vacuumizing, sealing, shrinking, and collecting the products through an idle roll conveyor, is defined as "in-line abuse resistance". Scope of this test is to provide a method to discriminate and rank bags of different structure at a laboratory level as to this aspect. The procedure to test this property is therefore devised so as to simulate as much as possible the most drastic conditions that might actually occur in the packaging lines. To perform this test, the bags to be examined are filled with metal blocks, vacuumized, sealed and shrunk on an industrial packaging line. The thus obtained packages are then checked for leakers and the in-line abuse resistance is evaluated by the % of rejects. Due to the harsh conditions purposely employed this number is typically high but, as indicated above, this test has not an absolute but only a relative meaning and its aim is to indicate whether a given structure is expected to have more or less abuse resistance of a standard bag used as comparison, when used at the customer plant.

The % Shrink, Haze, Gloss, Modulus, Tensile and Elongation of some representative structures of the present invention are reported on Table 1.

TABLE 1

Structure of						
20	Example no.	12	13	14	16	17
	% Shrink	72	81	85	89	88
	Haze	2.9	2.9	n.d.	n.d.	n.d.
	Gloss	109	104	n.d.	n.d.	n.d.
	Modulus					
25	LD	3780	4168	n.d.	n.d.	n.d.
	TD	3290	4226	n.d.	n.d.	n.d.
	Tensile					
	LD	930	968	n.d.	n.d.	n.d.

	TD	690	878	n.d.	n.d.	n.d.
Elongation						
	LD	165	200	n.d.	n.d.	n.d.
	TD	117	115	n.d.	n.d.	n.d.

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TABLE 1 continued

Structure of

Example no.	19	24	25	26	28
% Shrink	81	86	75	89	83
Haze	n.d.	3.4	4.3	3.5	n.d.
Gloss	n.d.	93.6	104	94.5	n.d.

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The results of the Puncture resistance and In-line abuse resistance tests for some representative structures of the present invention are reported in Table 2 below.

The bags used for the in-line abuse resistance tests were, 165 mm x 230 mm, end sealed bags. For comparative purposes the results obtained with a commercially available bag, 58  $\mu$ m thick, sold by Cryovac ® as BB4L, are reported in the last column on the right.

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TABLE 2

Structure of Example no							Cryovac®
	11	12	13	14	17	22	BB4L
Puncture							
(kg) 90°C	1.6	1.8	1.9	1.5	1.5	n.d.	0.5
In-line abuse							
% Rejects	n.d.	28	15	n.d.	n.d.	26	67

20

25

TABLE 2 continued

Structure of Example no						Cryovac®
	23	24	25	26	27	BB4L
Puncture						

(kg) 90°C	n.d.	1.3	1.4	1.3	1.5	0.5
In-line abuse						
% Rejects	41	70	26	74	70	67
n.d.=not determined						

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The sealing properties of some representative films of the present invention have been tested by evaluating the seal strength and the integrity of packages obtained by an overlapped sealing. An internal procedure has been developed to evaluate the ability of a heat-shrinkable bag to maintain seal hermeticity and integrity (i.e. no delamination) when submitted to a non-standard sealing cycle. As used herein "non standard sealing cycle" is intended to refer to the case where, in the packaging cycle, the bags filled with the product to be packaged are placed inside a vacuum sealing chamber machine mispositioned (i.e. at least partially overlapped). As indicated above, in an industrial packaging cycle, this may happen, in particular when the positioning of the bags in the vacuum sealing chamber is not controlled by an operator, or this may be done on purpose in order to increase the output per sealing cycle.

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This test on overlapped sealability has been carried out on a Cryovac® VSC 75 vacuum sealing machine set with a vacuum time of 20 s, a cooling time of 4 s, a sealing bar pressure of 1 bar and an adjustable impulse time. The test is a comparative test and the results obtained are compared to a standard that is represented by the same bag used however in a standard sealing cycle where the bag is correctly positioned inside the vacuum sealing chamber making sure that no overlap occurs, and the same sealing conditions are applied.

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In particular for each formulation two empty end-seal bags (260 mm width) obtained by transverse seal and cut of the oriented tubing, are placed in the center of the sealing bar overlapped one on the other by half of their width in order to simulate a non standard sealing cycle. The shrink bags are vacuumized and sealed at the pre-selected conditions. At the end of the cycle, the two shrink bags are slowly separated, one from the other, by tearing them apart along the seal seam. The seals are then visually checked for seal hermeticity and integrity (no delamination). The tests are then repeated at different impulse sealing times and the range of

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impulse times that allows to obtain reliable seals without rejects in case of non standard sealing cycle is determined. In Table 3 below, the minimum sealing impulse time (SIT min.) and the maximum sealing impulse time (SIT max.), i.e. the range of sealing impulse time at which the package hermeticity and integrity characteristics were maintained despite the non standard packaging cycle, are reported for some representative films according to the present invention.

TABLE 3

	Structure of Example no.	SIT min. (s)	SIT max (s)
	11	1.6	2.4
10	12	1.6	2.4
	13	1.4	2.4
	14	1.6	2.4
	15	1.6	2.4
	22	2.0	2.4
15	23	2.0	2.4
	24	1.6	2.4
	25	1.8	2.4
	26	1.6	2.0
	27	1.6	2.4

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## CLAIMS

1. A multi-layer heat-shrinkable film comprising at least  
a first outer heat-sealing layer (a) comprising one or more polyolefins;  
a second outer abuse layer (b) comprising a polyamide with melting point  $\geq 175^{\circ}\text{C}$ ; and  
5 an intermediate gas barrier layer (c) comprising PVDC.
2. The multi-layer heat-shrinkable film of claim 1 wherein the polyamide of the outer abuse  
layer (b) has a melting point of from about  $175^{\circ}\text{C}$  to about  $250^{\circ}\text{C}$ ; preferably of from  
about  $180^{\circ}\text{C}$  to about  $240^{\circ}\text{C}$ ; more preferably of from about  $185^{\circ}\text{C}$  to about  $230^{\circ}\text{C}$ ; and  
still more preferably of from about  $188^{\circ}\text{C}$  to about  $225^{\circ}\text{C}$ .
- 10 3. The multi-layer heat-shrinkable film of claim 2 wherein the polyamide of the outer abuse  
layer (b), with a melting temperature of from about  $188^{\circ}\text{C}$  to about  $225^{\circ}\text{C}$ , is selected  
from the group consisting of copolyamides 6/12, copolyamides 6/66, polyamide 6  
copolymers (modified polyamide 6) comprising less than 5 %, preferably less than 4 %,   
and even more preferably less than 3 % by weight of an aromatic co-monomer,  
15 copolyamides of polyamide 6 and a partially aromatic polyamide, and terpolyamides  
based on polyamide 6, polyamide 11, and polyamide 66.
4. The multi-layer heat-shrinkable film of claim 2 wherein the outer abuse layer (b)  
comprises at least 50 % by weight and preferably at least 60 % by weight of one or more  
polyamides with a m.p.  $\geq 175^{\circ}\text{C}$ , blended with an ethylene-vinyl alcohol copolymer.
- 20 5. The multi-layer heat-shrinkable film of claim 4 wherein the amount by weight of EVOH  
in the outer abuse layer (b) with respect to the overall weight of the layer is comprised  
between about 3 and about 40 % by weight, preferably between about 5 and about 35 %  
by weight, and even more preferably between about 10 and about 30 %.
6. The multi-layer heat-shrinkable film of claim 1 wherein the heat-sealing layer (a)  
25 comprises a single polyolefin or a blend of two or more polyolefins with melting  
temperature  $< 140^{\circ}\text{C}$ , preferably  $< 130^{\circ}\text{C}$ , and more preferably comprised between  $80^{\circ}\text{C}$   
and about  $128^{\circ}\text{C}$ .

7. The multi-layer heat-shrinkable film of claim 6 wherein the heat-sealing layer (a) comprises heterogeneous or homogeneous ethylene-(C<sub>4</sub>-C<sub>8</sub>)- $\alpha$ -olefin copolymers having a density  $\leq 0.915$  g/cm<sup>3</sup>, blends thereof with minor amount of polyethylene homopolymers, ethylene-vinyl acetate copolymers, ethylene-acrylic or methacrylic acid copolymers including ionomers, blends of heterogeneous or homogeneous ethylene-(C<sub>4</sub>-C<sub>8</sub>)- $\alpha$ -olefin copolymers having a density from about 0.915 g/cm<sup>3</sup> to about 0.930 g/cm<sup>3</sup> with ethylene-vinyl-acetate copolymers or ethylene-alkyl (meth)acrylate copolymers, ethylene-propylene-butene ter-polymers, ethylene-alkyl acrylate-maleic anhydride ter-polymers.
8. The multi-layer heat-shrinkable film of claim 7 wherein the heat-sealing layer (a) comprises a heterogeneous or homogeneous ethylene-(C<sub>4</sub>-C<sub>8</sub>)- $\alpha$ -olefin copolymer having a density  $\leq 0.915$  g/cm<sup>3</sup>, and preferably a heterogeneous or homogeneous ethylene-(C<sub>4</sub>-C<sub>8</sub>)- $\alpha$ -olefin copolymer having a density comprised between about 0.895 g/cm<sup>3</sup> and about 0.912 g/cm<sup>3</sup>.
9. The multi-layer heat-shrinkable film of claim 1 in the form of a seamless tubing wherein the outer heat-sealing layer (a) is the innermost layer of the tube.
10. A container obtained from a multi-layer heat-shrinkable film comprising at least  
a first outer heat-sealing layer (a) comprising one or more polyolefins;  
a second outer abuse layer (b) comprising a polyamide with melting point  $\geq 175$  °C; and  
an intermediate gas barrier layer (c) comprising PVDC,  
by a welding involving the outer heat-sealing layer (a), whereby said outer layer (a) is the inside layer of the container and the outer abuse layer (b) is the outside layer of the container.



# INTERNATIONAL SEARCH REPORT

Int. Application No

PCT/EP 99/07941

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 B32B27/08 B65D65/40

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 B32B B65D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

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X	EP 0 447 988 A (GRACE W R & CO) 25 September 1991 (1991-09-25) page 3, line 8 - line 57; claims 1,5-7,17; examples 11,17,19 ---	1,9,10
Y	EP 0 217 252 A (GRACE W R & CO) 8 April 1987 (1987-04-08) *comparative examples 5,6 * page 10; claims; examples 4-10; table III ---	1-3,6-10
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☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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- "A" document defining the general state of the art which is not considered to be of particular relevance
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# INTERNATIONAL SEARCH REPORT

Int. Application No

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